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CATALYTIC CRACKING OF DIESEL FUEL
FOR ARMY FIELD BURNERS

Part I
Feasibility of Producing Gaseous Fuel From Diesel Fuel
Via Catalytic Cracking

by
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This is one of three reports of a study to develop an advanced fuel conversion process to produce gaseous fuel for field burners. In this process, a gaseous mixture of light hydrocarbons is produced via the catalytic cracking of logistic fuels like diesel and JP-8. This innovative concept leads to a new generation of field burners which are relatively simple, reliable, easy to start and environmentally favorable. The objective of this report (Part 1) was to experimentally demonstrate the feasibility of a catalytic cracking process to produce hydrogen and light hydrogen molecules from diesel with a minimal yield of heavy hydrocarbon residues. The objective was fully met by successfully identifying state-of-the-art catalysts and processes, and experimentally demonstrating the feasibility of catalytic cracking of diesel to produce easily combustible gaseous fuel. A second report (Part II Natick/TR-00/005) contains results of objectives to demonstrate the long-term performance (durability/reliability) of a catalytic cracking process developed during Part I to produce a prototype catalytic burning unit. A third report (Part III Natick/TR-00/006) discusses results of the objective to develop a centralized fuel-processing unit for large scale multiburner operation utilizing the catalytic cracking technology.

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Preface

The study reported here was conducted under U.S. Army Soldier and Biological Chemical Command (SBCCOM), Soldier Systems Center, contract No. DAAK60-94-C-0030. The work was performed by Jae Ryu of Aspen Systems, Inc., Marlborough, MA. Mr. Donald Pickard of the Soldier Systems Center was the project officer for the contract.

This report is one of a series of three. The references for the other reports are:

Ryu, J., Zhou, A., Borhanian, H. (1995). *Catalytic Cracking of Diesel Fuel for Army Field Burners, Part II: Demonstration of Long Term Performance and Production of a Prototype Catalytic Cracking Unit* (Tech. Rep. NATICK/TR-00/005). Natick, MA: Soldier Systems Center, U.S. Army Soldier and Biological Chemical Command (SBCCOM).

Zhou, A., Borhanian, H. (1998). *Catalytic Cracking of Diesel Fuel for Army Field Burners, Part III: Study of Catalytic Cracking and Steam Reforming* (Tech. Rep. NATICK/TR-00/006). Natick, MA: Soldier Systems Center, U.S. Army Soldier and Biological Chemical Command (SBCCOM).

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CATALYTIC CRACKING OF DIESEL FUEL FOR ARMY BURNERS

Part I
Feasibility of Producing Gaseous Fuel Via A Catalytic Cracking Process

Executive Summary

The overall objective of this program is to develop an advanced fuel conversion process to produce gaseous fuel from diesel for field burners. In the proposed process, a gaseous mixture of light hydrocarbon molecules will be produced via the catalytic cracking of diesel. This innovative concept will allow the development of field burners which are relatively simple, reliable, and easy to start. Furthermore, the gaseous light hydrocarbons will promote clean combustion, which is environmentally favorable.

The objective of this three-phase program was to experimentally demonstrate the feasibility of a catalytic cracking process to produce hydrogen and light hydrocarbon molecules from diesel with minimal yield of heavy hydrocarbon residues. In Phase I, we fully met these objectives by successfully identifying the state-of-the-art catalysts and processes, and experimentally demonstrating the feasibility of catalytic cracking of diesel to produce easily combustible gaseous fuel. The conversion efficiency to light hydrocarbons (gaseous phase) was 80% and 70% for the reference fuel (cetane) and diesel, respectively. Furthermore, we demonstrated the clean combustion (blue flame) of the cetane and diesel fuel via catalytic cracking using an existing burner head.

In Phase II, we will design and fabricate a catalytic cracking unit to retrofit current Army vaporizing field burners. All necessary burner components, such as the nozzle and fuel lines will be modified and optimized accordingly. We will also demonstrate the reliability and durability of the newly developed catalytic cracking/burner units by conducting long term performance tests on diesel fuel. Finally, we will demonstrate the multi-fuel capability of the proposed system through the use of kerosene and DF-2 fuels. The catalytic cracking unit to be developed in Phases I and II will be suitable for individual field burners (about 60,000 BTU capacity).

If successfully developed, the proposed concept will have tremendous potential for an unlimited number of residential and commercial applications. For example, residential gas appliances (i.e., heating systems, stoves, grills, and clothes dryers) could be operated by the gaseous fuel produced from the fuel processing units. The benefits to this application would include increased energy efficiency and clean oil combustion, as well as the reduction of the length of gas transport lines and subsequently the risks associated with handling gaseous fuel. Similar advantages could be realized for commercial applications.

1. Phase I Technical Objectives

The key aspect of Phase I of this four phase program was to experimentally demonstrate the feasibility of a catalytic cracking process to produce hydrogen and light hydrocarbon molecules from diesel with minimal yield of heavy hydrocarbon residues. The specific objectives were:

- To identify state-of-the-art hydrocarbon cracking catalysts and processes from literature;

- To determine the efficiency of diesel conversion into light hydrocarbons (C_1 - C_5) using at least two commercial cracking catalysts;

- To determine the cracking product composition as a function of process conditions, such as catalyst temperature and fuel-to-catalyst ratio; and

- To fabricate and evaluate the performance of the breadboard diesel catalytic cracking unit using an existing burner head.

The achievements realized during Phase I (March 23 - November 23, 1994) will be discussed in the following sections.

2. Introduction

2.1. Background

Cracking of heavy hydrocarbons to produce light hydrocarbons has been practiced for almost two hundred years, and may be classified in two categories: thermal cracking and catalytic cracking. Thermal cracking involves many chemical reactions, including dehydrogenation, polymerization, and isomerization. However, the primary chemical reaction involves the formation of free radicals by the random loss of hydrogen atoms to other free radicals, followed by a carbon chain rupture to the hydrogen deficient carbon atom. Thus, many different carbon chain lengths are possible in the product from thermal cracking.

The use of catalysts to modify the yields and quality of cracked products was initiated as early as 1915 and was successfully commercialized in the 1930's. Since then, major efforts have been focused on the development of highly efficient catalysts and economical cracking processes[1-4] to increase the yields of valuable products such as high octane gasoline for the petroleum industry. In parallel, there has been a continued effort to produce synthetic fuel from coal utilizing the catalytic cracking process. Both syngas and liquid fuels have been commercially produced via catalytic cracking of tar.[5-8] The exact mechanism involved in catalytic cracking of hydrocarbons is not precisely known, although a staggering amount of research has been published on the effect of catalysts, operational variables, and feedstock quality on product yields just to name a few.

When cracking occurs, there is a hydrogen deficiency in the reaction and complex reactions follow to reconcile the unsaturated light hydrocarbons (light olefins). Reactions that may occur include polymerization, formation of aromatic hydrocarbons, and coking. Most of these secondary reactions of light olefins are undesirable and reduce the yield of gaseous products. The degree of these secondary reactions, which will determine the product distribution in the cracking process, depends heavily on process conditions. Furthermore, addition of various cracking promoters or product stabilizers, such as water, air, or hydrogen (recycled from the product stream), can significantly suppress the above-mentioned secondary reactions. However, supplying water to the fuel conversion process may be logistically unfavorable for certain Army field operations, and air injection or recycling hydrogen product may require power.

As mentioned above, catalytic cracking of heavy hydrocarbons to produce light hydrocarbons is a well established process in the petroleum and coal industries. However, the specific process of catalytic cracking of diesel to produce light hydrocarbons has not yet been investigated. There have been intensive but less than fruitful research efforts within the U.S. military to produce hydrogen via reforming of diesel. The purpose of these programs was to provide electricity utilizing phosphoric acid fuel cell (PAFC) technology at remote sites.[9,10] As a result of these efforts, various reforming processes have been successfully developed to produce hydrogen-containing gas mixtures from diesel through slight modification of well-developed industrial processes.

Independently, there has been a worldwide effort to develop an onboard fuel processing unit for production of gaseous fuels from liquid hydrocarbons in order to minimize air pollution from internal combustion engines for automobiles.[11] For this application, the gaseous product typically comprised of mostly hydrogen with a small amount of hydrocarbon impurity. As a result of this program, advanced catalysts and catalytic cracking processes were successfully developed. However, for the internal combustion engine, the requirements in fuel product distribution were rather stringent, and therefore, the onboard fuel processor for automobiles has not been realized. Currently the worldwide concerns on clean environment have re-ignited the interest in onboard fuel processors for a zero emission vehicle.

2.2. State-of-the-art Catalysts for Catalytic Cracking of the Heavy Hydrocarbons

As discussed in the previous section, catalytic cracking of heavy hydrocarbons is a well developed and routine process in the petroleum industry. For industrial processes, the catalysts and catalytic reaction processes are usually designed to promote specific chemical reactions to achieve a high yield of specific products (high selectivity). The process conditions for the industrial catalytic cracking of the heavy hydrocarbons are generally: reactor temperatures above 900°F (480°C) and reactor pressures higher than 700 psi. Most of cracking catalysts are designed to be used in these conditions for higher yield of high octane gasoline. Therefore, these well-developed industrial catalysts was not suitable for the current program.

As the Phase I research started, we began to collect information on catalytic cracking of hydrocarbons through nationwide computer data based search (through NERAC, Inc.) and Engineering Index and Chemistry Abstract library search at MIT and Tufts University to identify

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suitable catalysts for this program. These searches were conducted with the following essential requirements for the catalysts:

- Catalysts should exhibit excellent activity at lower reactor temperatures and ambient pressure; (near 1 atm);
- Catalysts should promote light hydrocarbon production ($C_1 - C_4$); and
- Catalysts should be highly tolerant to catalyst poisoning such as coking.

As a result of the literature search, we collected an extensive amount of information on the recent research activities for the catalytic cracking of paraffinic hydrocarbons over the zeolite-based catalyst.[12-25] These catalysts, such as HY-zeolite or ZSM-5 zeolite, have been used to produce high yields of lighter hydrocarbons ($C_1 - C_4$) at relatively moderate process conditions. An example of this work is shown in Fig. 1, reported by Guerzoni and Abbot.[14] As shown in Fig. 1, a majority of the products in the catalytic cracking of heavy hydrocarbons ($C_{12} - C_{18}$) over the HY- and HZSM-5 zeolite catalysts were $C_2 - C_4$ at catalyst temperature of 400°C and 1 atm. Furthermore, a literature review indicated that the catalytic cracking activities increased significantly with an increase in carbon numbers in the hydrocarbon feedstock (see Fig. 2).[12] Considering that the major components in diesel fuel are cetane (n-hexadecane) and 2,2,4,4,6,8,8-heptamethylnonane (HMN), it would be relatively easy to catalytically crack the diesel fuel.

During Phase I, we have acquired and tested many different kind of catalysts for this program (see **Table 1.** for the list of catalysts we tested). In summary, we successfully identified suitable catalysts after extensive literature searches and have acquired these catalysts for evaluation. In the following section, we will describe the results of catalytic cracking experiments using these catalysts.

3. Results and Discussions

3.1. Catalytic Cracking: Experiments

Experimental Setup

The main thrust of Phase I of the proposed research is to experimentally demonstrate the feasibility of a catalytic cracking process to produce light hydrocarbon molecules from diesel for easy combustion. For this experiment, we established a fixed bed catalyst reactor setup, as shown in Fig. 3 (schematic) and in Fig. 4 (picture). This setup consisted of: (1) fuel feed system; (2) reactor unit; (3) heavy hydrocarbon condenser unit; and (4) gas flow meter and exhaust.

The fuel was gravity fed and flow rates were controlled by using a pre-calibrated liquid rotameter. The reactor unit consisted of a quartz glass catalyst bed (1 inch OD and 12 inches long), a high temperature ceramic heater (6 inches long), a glass tube fuel level indicator, a pre-heater tape, and tape heaters for effluent stream heating. Temperature of the reactor was controlled by using a programmable temperature controller and a type K thermocouple located on the outside of the reactor tube. The temperature of the catalyst bed was monitored using a type K
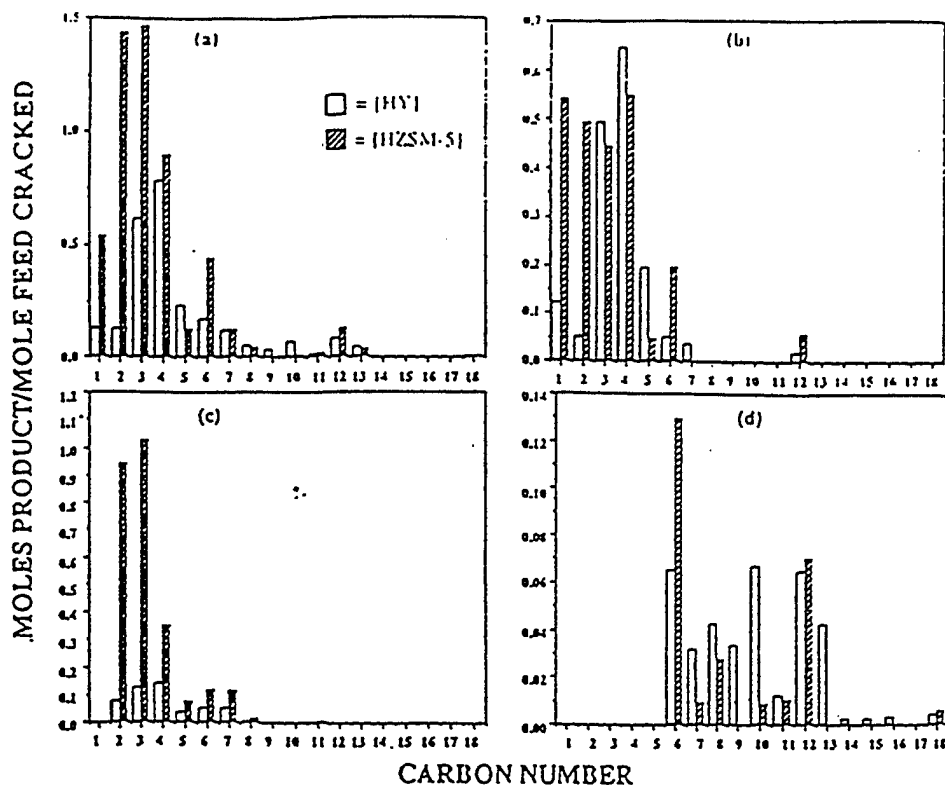
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Figure 1: Product Distribution from Catalytic Cracking of Heavy Hydrocarbons over HY and HZSM Zeolite Catalysts at 400°C. (a) Total Hydrocarbons; (b) Paraffins; (c) Olefins; and (d) Aromatics.[14]
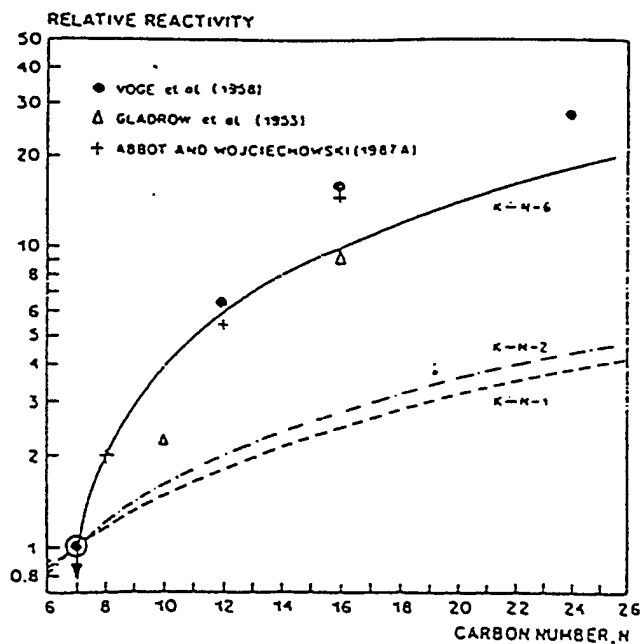
Figure 2: Comparison of the Effects of Carbon Number on Cracking Reactivity Expressed as Reactivities Relative to that of n-Heptane.[12]

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Table 1. List of Catalysts Tested in Phase I and Their Specifications

Catalyst	Manufacturer	Size	Active Agents	Feedstock	Product	Remark
HYC-642	Acreon	1/16"	Ni-Mo	GO, VGO	Kero., GO	Tested
HYC-652	Acreon	1/16"	Ni-Mo	GO, VGO	Naphtha, Kero.	Tested
HPC-50	Acreon	1/20"	Ni-Mo	VGO, HVGO	FCC, HC feed	Tested
HTH-548	Acreon	1/20"	Ni-Mo	HGO	Hydro-conversion	Tested
TK-550	Haldor Topsoe	1/16"	Co-Mo	Naphtha to VGO	HDS	Tested
TK-551	Haldor Topsoe	1/16"	Ni-Mo-P	VGO	Diesel, FCC feed	Tested
HZSM-5	United Catalysts	1/16"	HZSM-5 zeolite	Experimental catalysts	-	Tested
HY	United Catalysts	1/16"	Y zeolite	Experimental catalysts	-	Tested
LZY-84	UOP Catalysts	1/16"	Y-zeolite	Experimental catalysts	-	Tested
LZY-210	UOP Catalysts	1/16"	Y-zeolite	Experimental catalysts	-	Tested
LZM-8	UOP Catalysts	1/16"	Mordenites	-	-	To be Tested
MFI	UOP Catalysts	1/16"	Silicalite	-	-	To be tested
CBV400	PQ Corp		Y Zeolite	Experimental catalysts		Not a suitable shape for our reactor system
CBV1502	PQ Corp		Z Zeolite	Experimental catalysts		Not a suitable shape for our reactor system

Figure 3: Schematic of the Catalytic Cracking Experiment Setup

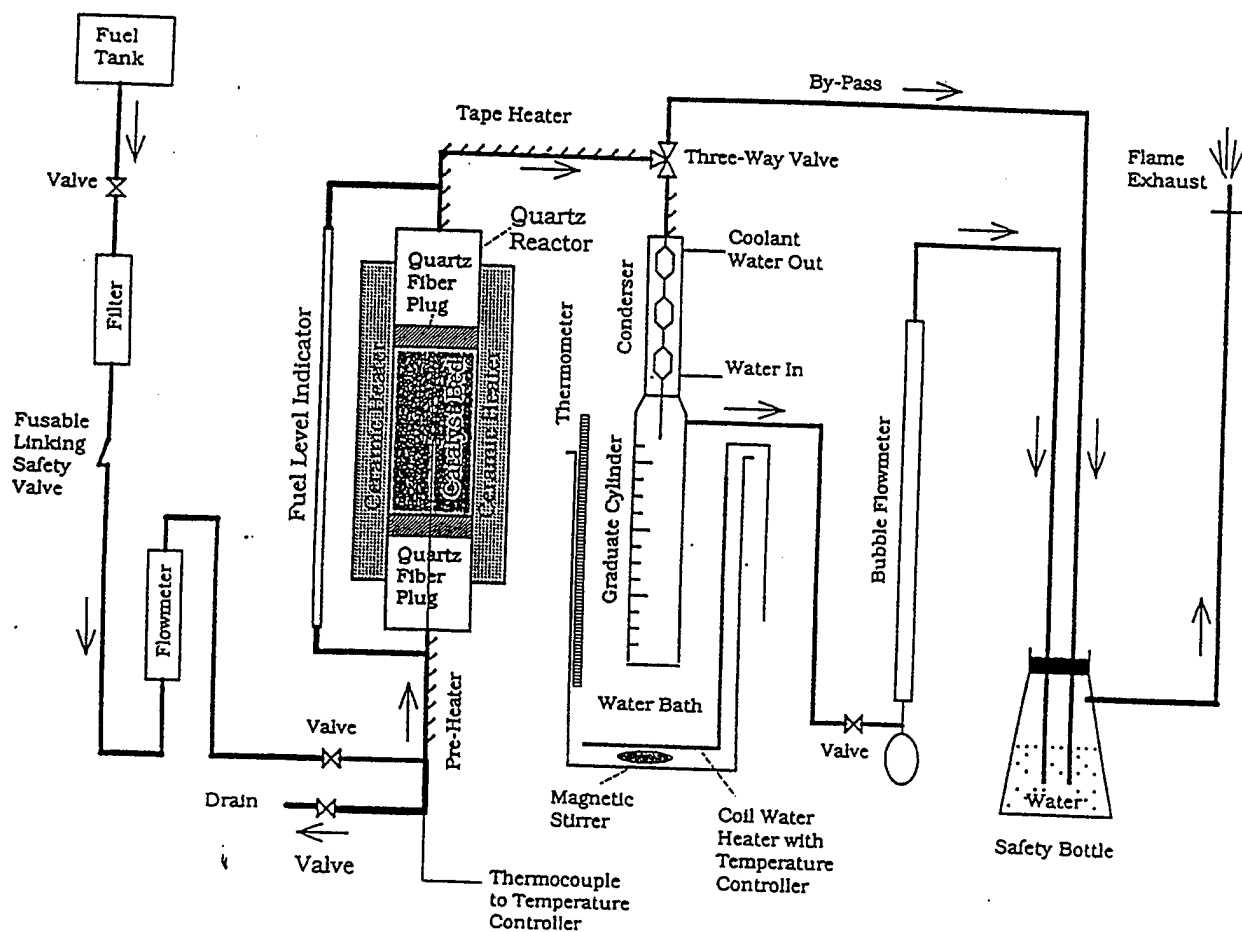thermocouple imbedded into catalysts and a temperature monitor. The fuel level indicator, which was made of 22 mm ID Pyrex tube, was added to the setup during catalyst screening tests. This addition was absolutely necessary to monitor the position of the fuel within the catalyst bed and to control fuel feed rates during continuous feed cracking experiments.

The catalyst bed temperature (determined by the ceramic heater temperature) is the most important variable in the catalytic cracking experiments. During the catalyst screening tests, the reactor temperatures were set at 300°C (572°F), 350°C (662°F) and 400°C (752°F). For noncontinuous fuel flow experiments, the catalyst bed temperatures were almost the same as the reactor set temperatures (within 3°C). For continuous fuel flow experiments, however, the catalyst bed temperatures were 60-100°C (140-212°F) lower than those of reactor set temperatures. For example, when the reactor set temperature was 366°C (690°F), the catalyst bed temperature was measured to be 264°C (507°F) for continuous fuel flow catalytic cracking experiment. The large temperature discrepancy in the continuous flow cracking experiments may indicate the large endothermic heat required for the cracking of hydrocarbons.

Temperatures for the tape preheater and effluent line heater were controlled using variable power supplies, and monitored by using type K thermocouples and temperature indicators. For catalyst screening tests (generally noncontinuous fuel flow experiments), the preheater temperature was set at 270°C (518°F). For continuous fuel flow experiments, the preheater temperatures were varied between 240-311°C (464-592°F). The temperature of effluent
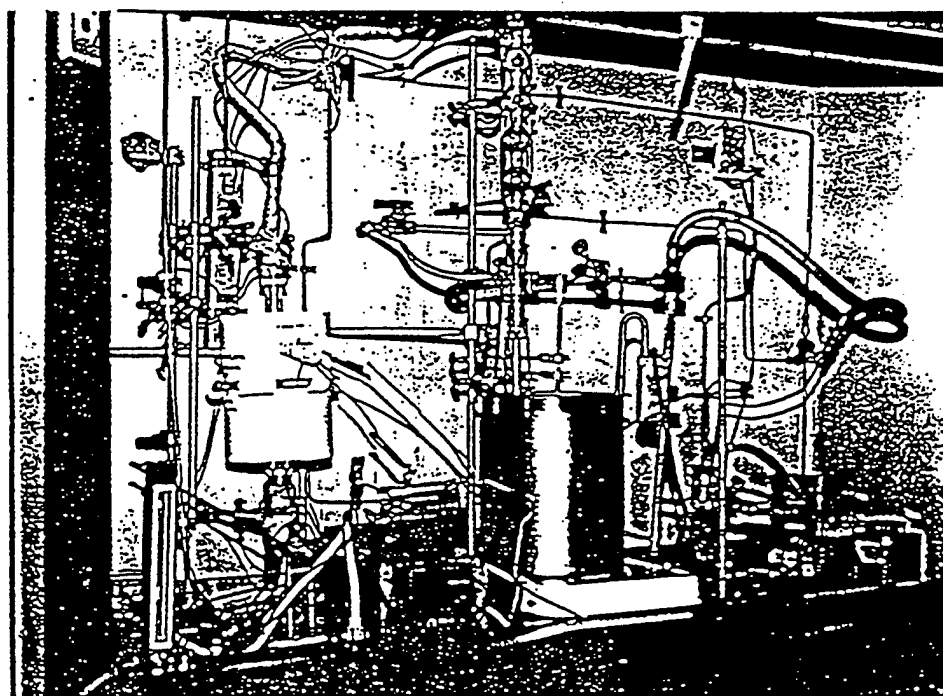

Figure 4: Picture of the Catalytic Cracking Experiment Setup

gas line was set at 250°C (482°F), which is much lower than boiling point of the n-hexadecane (287°C=549°F). Therefore, most of the fuel vapor (uncracked) was condensed at the effluent gas line and dripped back to the reactor tube.

The effluent gas stream from the catalyst reactor was introduced to a condenser unit, which consisted of a water cooling condenser and a graduated cylinder liquid collector. The temperature of the cooling water was about 20°C (tap water) and the graduated cylinder liquid collector was immersed into an isothermal bath whose temperature was kept at less than 2°C using ice during liquid collection mode operation. All the heavy hydrocarbons (heavier than butane), we believe, were captured and condensed in the collector. Therefore, constituents in the effluent gas stream from the condenser unit would be only permanent gas or light hydrocarbons (lighter than butane). The outlet of the condenser unit is connected to the bubble flower meter to measure the flow rate of the gaseous phase from the catalytic cracking reactor. The effluent gas stream passes through a water safety bottle and vents through flame exhaust.

3.2. Catalytic Cracking of Reference Fuel (Cetane)

The main technical objective during this task was to identify suitable catalysts and demonstrate the feasibility of the proposed concept of the catalytic cracking of diesel reference fuel. As discussed previously, a host of catalysts (many hundreds of different family) have been developed and used for the petroleum industry. However, most of these catalysts were designed to be used at specific process conditions with high selectivity for the specific product. Therefore, it is reasonable to assume that no catalyst has been developed for the process conditions and product requirements of the proposed program. With the limited resources and time, we cannot develop new type of catalysts for the proposed program.

Our approach to overcome this technical barrier was to select catalysts based on our previous experiences in general catalysis and the results of the published research. Once suitable catalysts were identified and acquired, we quickly tested these catalysts using the test conditions listed in **Table 2.** (catalysts screening tests). For certain catalysts, diesel to gaseous fuel cracking rate was too slow to conduct continuous fuel (feedstock) flow experiments. For consistency in test conditions, therefore, we used noncontinuous fuel flow methods for screening tests. When suitable catalysts were identified from screening tests, process optimization was followed. For the process optimization experiments, we used continuous fuel flow test conditions.

3.2.1 Catalysts Screening Tests

Results of catalysts screening tests are summarized in **Table 3.** and plotted in **Fig. 5.** As shown in this table and figure, the cracking performance of the catalysts varies widely depending on the type of catalyst. For example, catalyst TK-551 (Haldor Topsoe), which has been successfully used for steam reforming of diesel to produce hydrogen, performed very poorly for the catalytic cracking of the reference fuel. Meanwhile, catalyst HZSM-5 (United Catalysts), which has been developed as an adsorption agent for pollutants, performed the best among all catalysts tested.

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Table 2. Catalyst Screening Test Conditions

Reactor Temperature (°C)	Preheater Temperature (°C)	Effluent Stream Heater Temperature (°C)	Amount of Catalysts (gram)	Fuel Conditions
300, 350, & 400	270	250	30	21 cm³ of hexadecane (batch process)

These results indicate that zeolite-based catalysts performed better than other families of catalysts. Therefore, we investigated extensively zeolite-based catalysts in this program. Whenever we acquired new catalysts, we quickly evaluated them using catalyst screening test procedures.

3.2.2. Process Optimization Experiments

Once suitable catalysts were identified in the screening tests, we started process optimization. Among the catalysts listed in **Table 2.**, catalyst HZSM-5 was the most promising. The important process parameters considered in the process optimization experiments include the following:

- fuel flow rate (determine the maximum fuel flow rate achievable);
- reactor and catalyst bed temperatures; and
- preheater temperature.

Results of the catalytic cracking of reference fuel, n-hexadecane, over the HZSM-5 catalyst are summarized in Fig. 6 a, b, & c. The liquid fuel (n-hexadecane) flow rate as a function of the preheater temperature is shown in Fig. 6a for the reactor temperatures at 315°C (599°F) and 366°C (691°F). Throughout the experiment, we tried to maintain the liquid fuel level, which was determined by the fuel flow rate and the fuel consumption rate via catalytic cracking, at about 1 inch above the bottom of the catalyst bed. If fuel flow rate was much greater than fuel consumption rate, liquid fuel level increased and, eventually, all the catalysts were immersed into the fuel (flooding). If fuel flow rate was low compared to the fuel consumption rate, the catalyst bed dried out and cracking reaction slowed down. In either case, cracking occured, but for consistency, we tried to maintain the same fuel level in continuous flow experiments.

When the preheater temperature is high, the fuel flow rate would increase because of rapid consumption of liquid fuel or higher rate of cracking at the catalyst bed. The effect of preheater temperature on fuel flow rate is clearly shown for the test with reactor temperature at 366°C. However, for the test with reactor temperature at 315°C, the effect of the preheater temperature on fuel flow rate is negligible.

The effect of preheater temperature on the catalyst bed temperature is shown in Fig. 6b. As shown in this figure, the catalyst bed temperature is about 60 and 100°C lower than that

Table 3. Results of Catalyst Screening Tests

Manufacturer of Catalyst	Type of Catalyst	Length of Catalyst Bed (inch)	Reactor Temperature (°C)	Gas Flow Rate (cm³/min.)	Catalyst ID Number
United Catalysts	HZSM-5	4 1/2	400	116.4	CAT. 024
		4 1/2	350	89.2	CAT. 025
		4 1/2	300	43.1	CAT. 026
Acreon	HYC-642	4 1/8	400	21.3	CAT. 006
	HYC-642	4 1/8	350	14.5	CAT. 005
	HYC-642	4 1/8	300	2.6	CAT. 004
Acreon	HYC-652	4	400	12.9	CAT. 007
	HYC-652	4	350	7.2	CAT. 008
	HYC-652	4	300	2.5	CAT. 009
Acreon	HTH-548	4	400	25.0	CAT. 010
	HTH-548	4	350	10.0	CAT. 011
	HTH-548	4	300	0.7	CAT. 012
Acreon	HPC-50	4 1/4	400	20.6	CAT. 013
	HPC-50	4 1/4	350	12.6	CAT. 014
	HPC-50	4 1/4	300	1.7	CAT. 015
Haldor Topsoe	TK-551	4 3/8	400	10.2	CAT. 016
	TK-551	4 3/8	350	2.6	CAT. 017
	TK-551	4 3/8	300	1.7	CAT. 018
Haldor Topsoe	TK-550	4 1/4	400	9.0	CAT. 019
	TK-550	4 1/4	350	4.3	CAT. 020
	TK-550	4 1/4	300	0.3	CAT. 021

of the reactor for reactor temperature of 315 and 366°C, respectively. Such large discrepancy between the reactor temperature and the catalyst bed temperature can be attributed to the large endothermic heat of catalytic cracking. The relationship between catalyst bed temperature and reactor temperature is a very important parameter to properly design a cracking unit for field burners.

The effluent cracked gas (butane or lighter hydrocarbons) flow rate as a function of preheater temperature is shown in **Fig. 6c.** As we expected, the product gas flow rate increases with an increase in reactor or preheater temperature. A technical goal of the optimization experiments is to identify process conditions where we can achieve high gas product flow rate (high cracking conversion efficiency) at reasonably low reactor and preheater temperatures.

Results of the investigation to determine the boiling point of the liquid residue in the condenser are presented in **Fig. 7.** The data were obtained by measuring the volume of the liquid residue in the collector bottle as the water bath temperature increased from 2°C to 98°C. As shown, the volume of the liquid residue continuously decreased with the increase in the water bath temperature. However, more than 63% of liquid still remained in the collector bottle after heating it to 98°C. Although this experiment was not conducted in steady-state conditions (slow but continual heating, therefore, it was not in thermodynamic equilibrium), this result indicated that a large portion of the liquid residues has boiling points higher than 98°C.

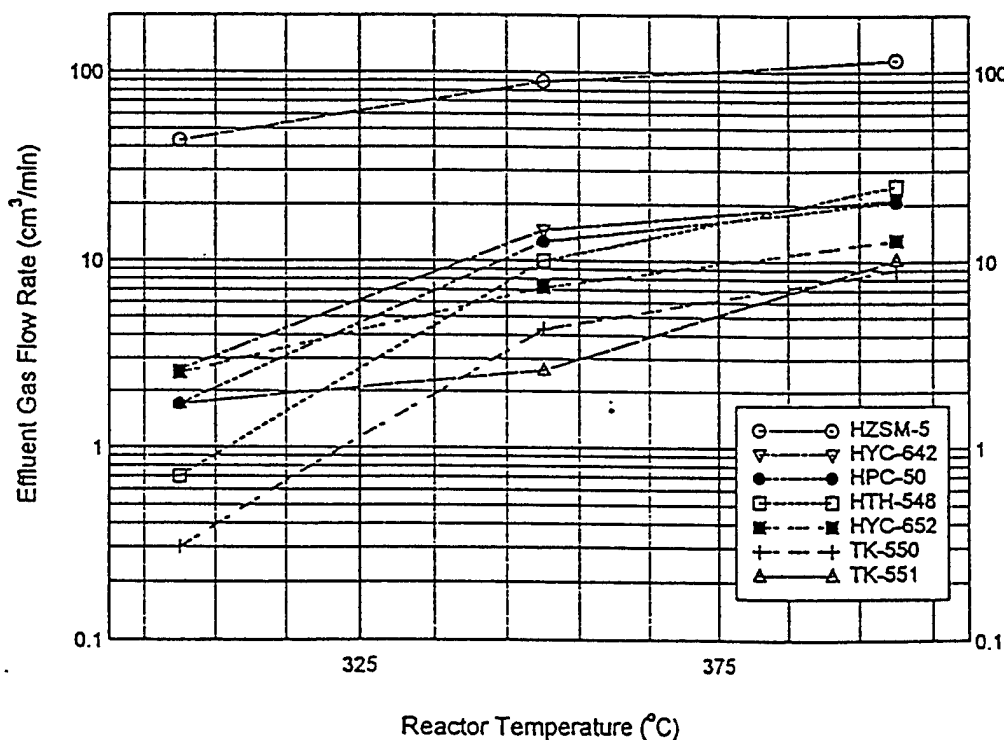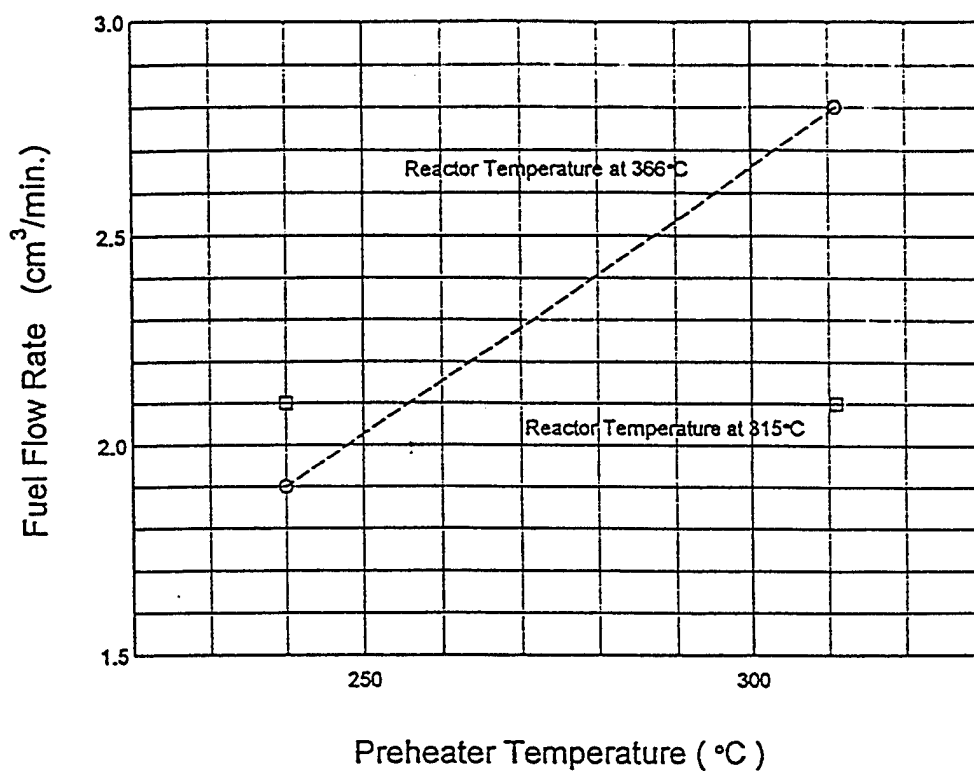**Figure 5: Effluent Gas Flow Rates as a Function of Reactor Bed Temperature for the Different Catalysts Tested.**

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(a)
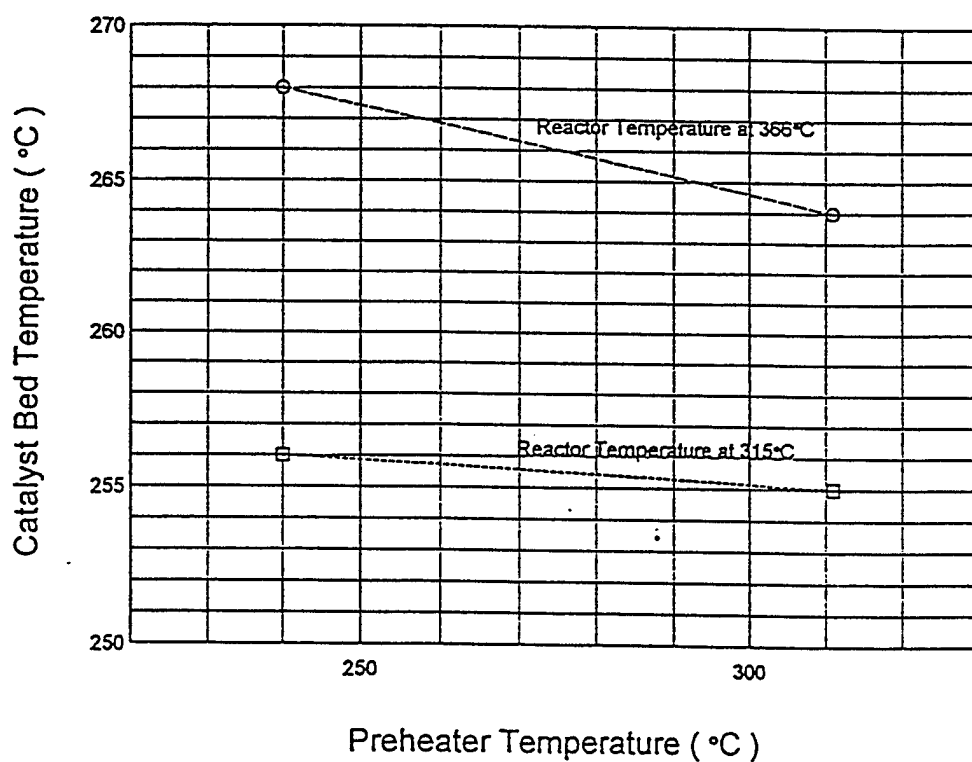
(b)

Figure 6:   Results of Catalytic Cracking of n-Hexadecane Over HZSM-5 Catalysts with Continuous Fuel Flow. (a) Fuel Flow Rate; (b) Catalyst Bed Temperature; and (c) Effluent Gas Flow Rate as a Function of Preheater Temperatures.

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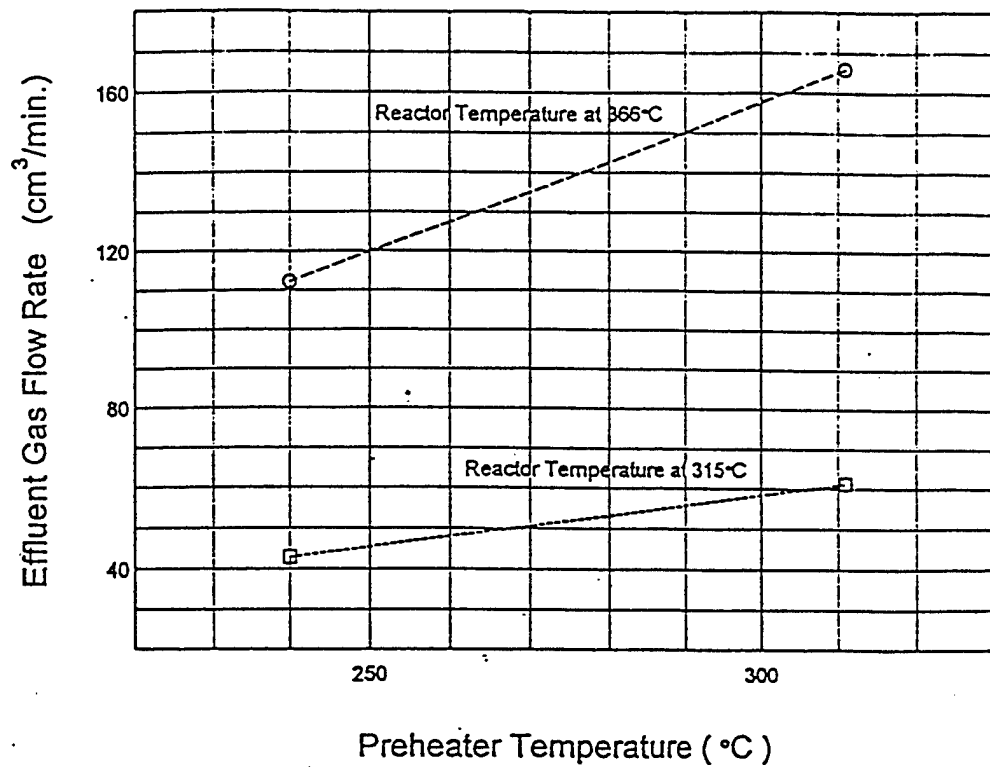
(c)

Figure 6: Results of Catalytic Cracking of n-Hexadecane Over HZSM-5 Catalysts with Continuous Fuel Flow. (continued)
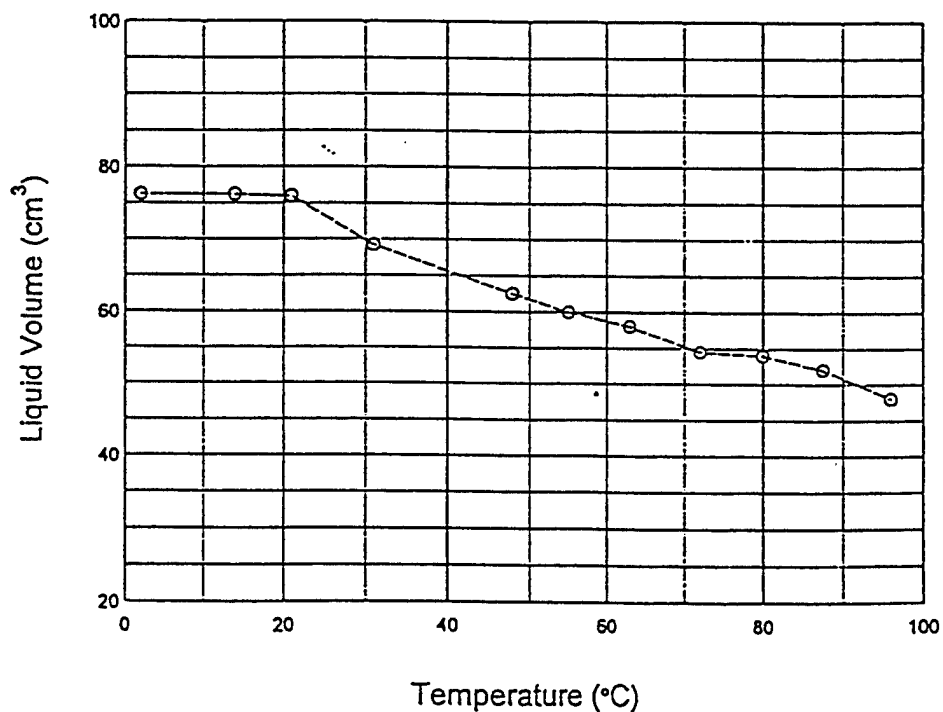

Figure 7: Changes in Volume of Liquid Residue with Continuous Increase in Water Bath Temperature.

3.2.3. Cetane Fuel Conversion Efficiency

In catalytic cracking process optimization experiments, we found that the preheater temperature of 200°C (392°F) and the reactor temperature of 350°C (662°F) were suitable for catalytic cracking of the reference fuel (cetane) over the HZSM-5 catalysts. The fuel conversion efficiency was determined using these process conditions at various fuel flow rates.

In this experiment, when the reactor conditions and the fuel flow rate reached steady-state, the effluent stream from reactor was introduced to a cold trap whose temperature was maintained at near 0°C. In this condition, hydrocarbons with boiling point above 0°C ($>C_5$) were condensed and accumulated in a graduate cylinder (condenser bottle) in the cold trap and the gas phase light hydrocarbons (lighter than butane) were sent to the exhaust burner. After collecting liquid phase for a certain time period (the duration of cold trap operation is dependent upon the liquid phase accumulation rates), the liquid phase in the condenser bottle was heated to 100°C (212°F). Then the volume of the liquid residue in the condenser bottle was measured to determine conversion efficiency.

The conversion efficiency was determined using mass balance (see equation 1) between amount of fuel feed (fuel flow rate times period of cold trap operation) and amount of liquid remaining in the condenser bottle after heating the condenser bottle to 100°C. Therefore, in this program, we determined the efficiency of cetane or diesel conversion to heptane (C_7) or lighter hydrocarbons.

$$\text{Conversion Efficiency (\%)} = \left(1 - \frac{V}{F \times t}\right) \times 100 \qquad (1)$$

where F is the fuel flow rate (CC/min), t is the period of cold trap operation (min), and V is the volume of the remaining liquid in the condenser bottle after heating it to 100°C and measured at room temperature (CC). In this calculation, we assume that density of the liquid fuel and the liquid residue in the condenser are the same.

Results of this experiments are summarized in Fig. 8. For cetane, the fuel conversion efficiency was between 70 and 80 % at the preheater and reactor temperatures of 200 and 350°C, respectively.

3.3. Catalytic Cracking of Diesel Fuel

For this experiment, we purchased commercial diesel fuel from a gas station. The specifications of this diesel fuel are given in **Table 4.** This diesel fuel has a cetane number of 40 which means it is composed of about 30% cetane (n-hexadecane) and 70% 2,2,4,4,6,8,8-heptamethylnonane (HMN). This commercial diesel fuel also contains sulfur and trace amounts of many additives such as ignition improver, stability improver, corrosion inhibitor, etc..

Results of diesel catalytic cracking over the ZSM-5 catalysts are shown in **Fig. 9.** Overall, the fuel conversion efficiency was slightly lower in diesel (between 55 and 67%) compared to cetane (70 to 80%) at the same cracking conditions.

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4. Proof-of-Concept Testing

For proof-of-concept testing, we use both technical grade cetane (C_{17}) reference fuel and commercial diesel fuel (Exxon No. 2-D diesel). In this experiment, cetane was gravity fed and diesel was supplied using an M-3 burner fuel tank at 20 psi pressure. The key aspect of this experiment was to demonstrate the clean combustion of the produced gaseous fuel using an M-3 burner head.

4.1. Experimental Setup

For this experiment, the cracking experiment setup (shown in Fig. 3) was slightly modified to use pressurized diesel fuel (see Fig. 10). This included: (1) replacing the quartz reactor tube with a stainless steel tube (0.68 inch ID) and the corresponding O-ring seal joints with metal seal joints; (2) replacing fuel supply flowmeter to achieve a high fuel feed rate and less pressure drop at the fuel control valve; (3) removing glass fuel level indicator; and (4) attaching the M-3 burner head for combustion tests. The new fuel flowmeter (OMEGA Model No. FL-1953) was not calibrated for diesel fuel. Therefore, we determined the actual diesel fuel flow rate as a function of the flowmeter reading, as shown in Fig 11.
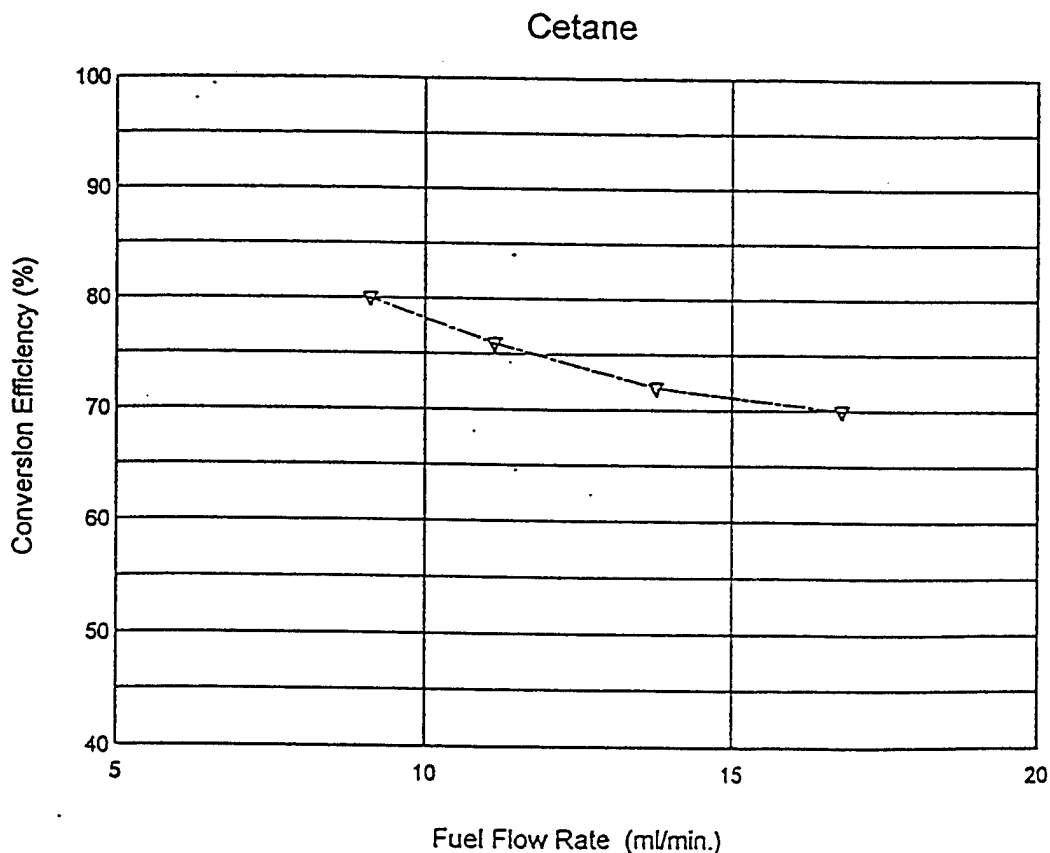

Figure 8: Cetane Fuel Conversion Efficiency as a Function of Fuel Flow Rate. Reactor and Preheater Temperatures of 350°C and 200°C, Respectively.

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Table IV: Specifications of the Commercial Diesel Fuel Used (Exxon No. 2-D).

Cetane Number	40
Flash Point, °C (°F)	52 (125)
Water and sediments, % vol	0.05
Distillation Temperature (90% vol. recovered), °C (°F)	338 (640)
Kinematic Viscosity, mm²/sec at 40°C	1.9 - 4.1
Ash %	0.01
Sulfur %	0.05

4.2. Results

Using the modified experimental setup, Aspen Systems clearly demonstrated the catalytic cracking of both the reference fuel (cetane) and commercial diesel fuel into gaseous fuel. Army Technical Program Officer (Mr. Don Pickard) was present at the final demonstration, where blue flame, clean combustion was demonstrated on the M-3 burner head for both cetane and diesel fuel. Once the reactor temperature reached stead state, the flowmeter valve was fully opened and the size of flame (heat output) was controlled using a needle valve in the burner head.
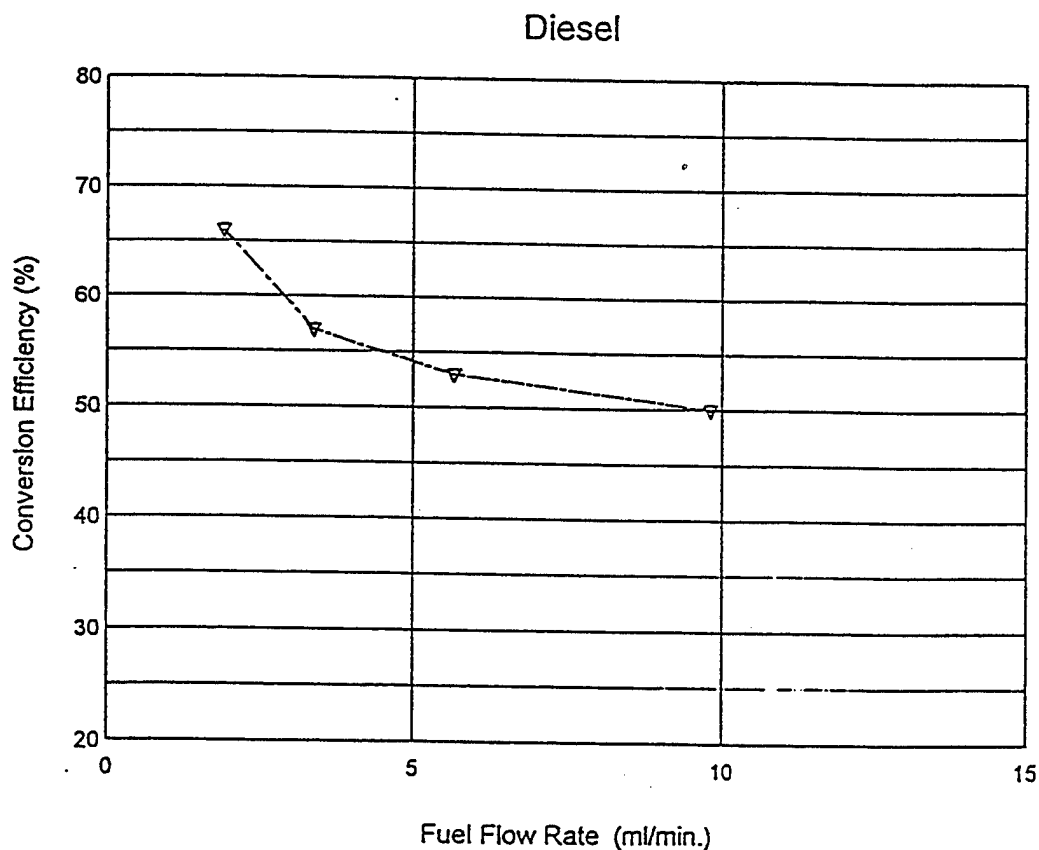

Figure 9: Diesel Fuel Conversion Efficiency as a Function of Fuel Flow Rate. Reactor and Preheater Temperatures of 350°C and 200°C, Respectively.
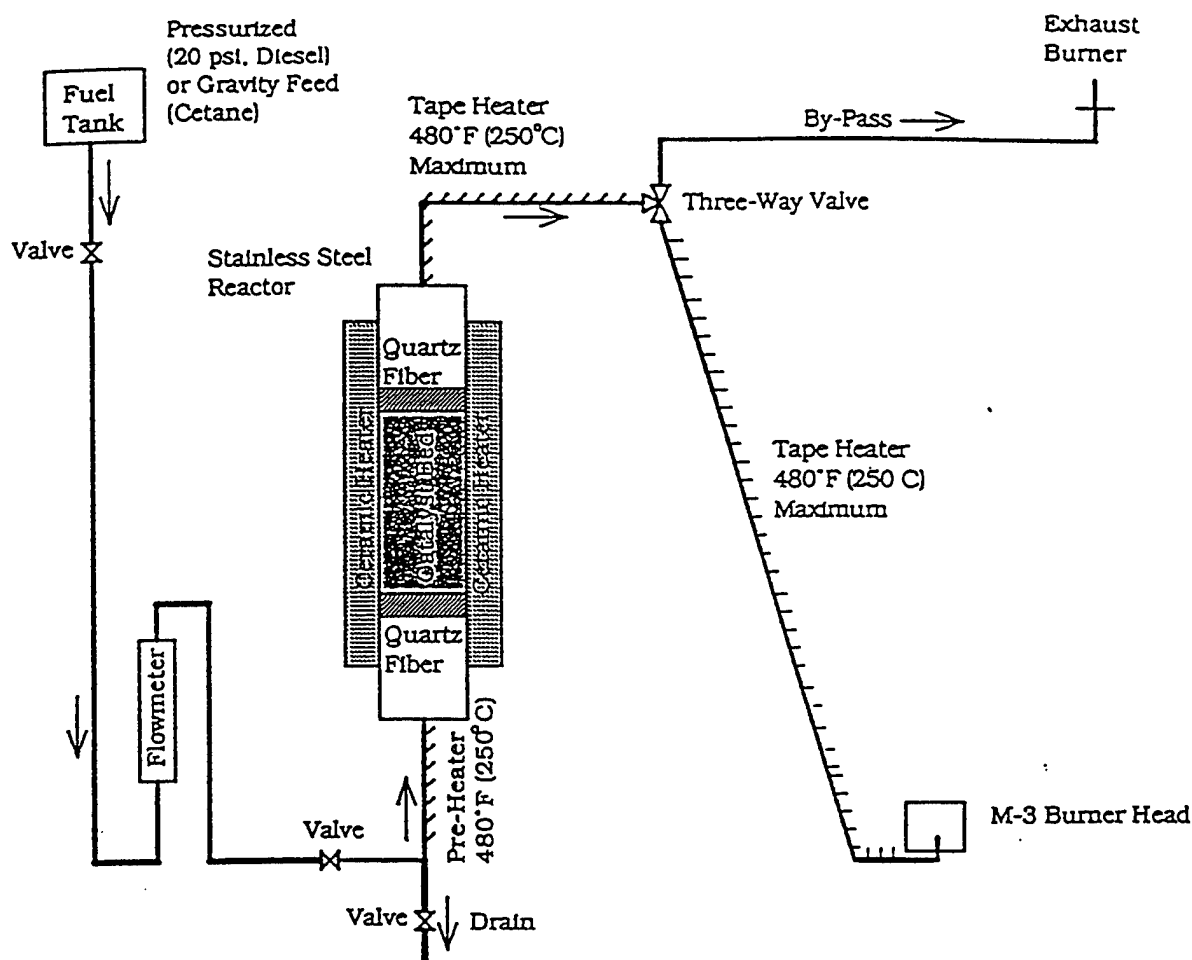
17

Figure 10: Schematic of the Catalytic Cracking Unit for Proof-of-Concept Testing
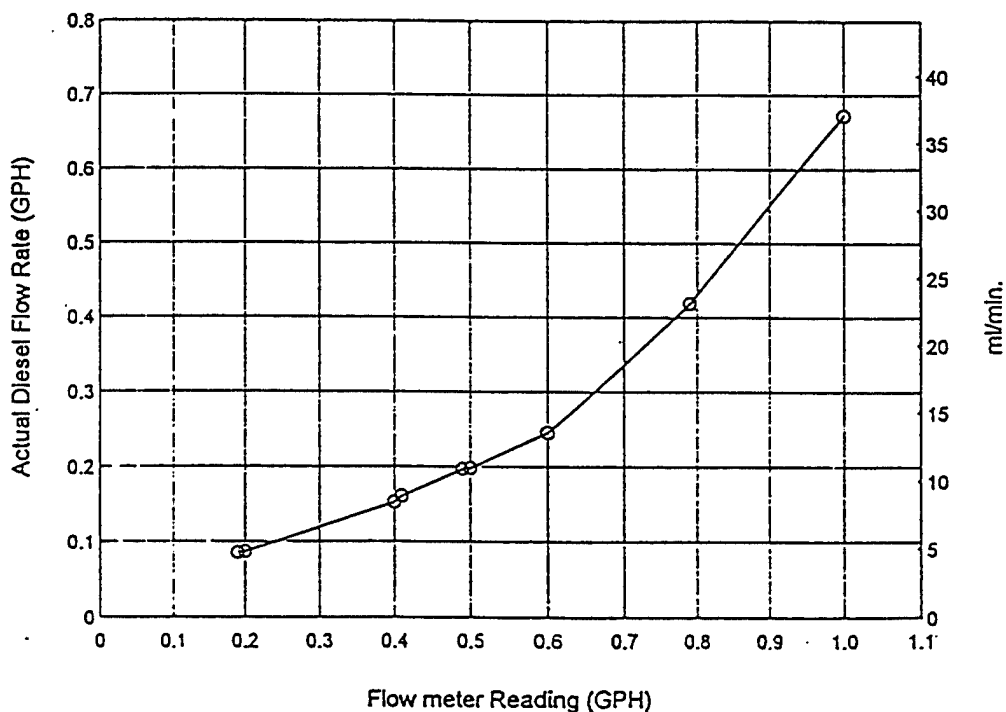

Figure 11: Calibration Curve of the Low Pressure-Drop Flowmeter for Diesel Fuel Used in the Proof-of-Concept Testing. (at Room Temperature)

For cetane, the effluent gaseous stream did not require to be heated to high temperatures to prevent condensing of gas phase. Liquid phase was not detected around the nozzle when effluent gas transport line (about 4 feet long) temperature was maintained above 150°C (302°F). At the gas line temperatures lower than 150°C (302°F), liquid phase began to build up around the nozzle. For Diesel, the gas transport line temperature had to be maintained above 220°C (428°F) to prevent liquid phase build up around the nozzle. In any case, the gas transport line temperature was significantly lower than the diesel boiling point (288°C, 550°F).

5.   Gas Chromatography

In this program, a gas chromatograph (GC) was employed to determine the composition of by-products from the catalytic cracking reaction. In GC operation, the substance to be analyzed (sample) is carried through the column by an inert gas (carrier gas). In the column, the sample mixture is partitioned between the carrier gas and a non volatile solvent (stationary phase) supported on an inert size-graded solid (solid support). The solvent selectively retards the sample components, according to their distribution coefficient, until they form separate bands to leave the column in the gas stream and are recorded as a function of time by a detector.

Positive identification of the numerous peaks emerging from GC columns for a complex mixture of analytes (chemical compounds) is very difficult. However, the unique gas-solid reactions between analytes and column packing material or capillary columns make this identification process possible. In the GC operation, the volume of carrier gas required to elicit a compound from the GC column is called the retention volume. Under constant pressure conditions, the flow rate is linear with time and, therefore, the retention volume is proportional to the retention time. This retention volume or time is characteristic of the sample and the liquid phase in the column, and can therefore be used to identify the chemical compounds. As such, chromatographic identification is based on a comparison of the retention time of the unknown component with that obtained from a known compound (standard sample) analyzed under identical conditions.

For GC analysis, we leased a GC system (HP model No. 5890 A) which is equipped with thermal conductivity detector (TCD) and flame ionization detector (FID). Since the by-products of the catalytic cracking reaction potentially have a wide ranges of product distribution, for example, from hydrogen and methane (C_1) to vaporized diesel (C_{17}), we can separate these products using a one column or one analysis process. Therefore, we had to separate these samples (by-products) in two categories which are gaseous samples taken after passing a cold trap (at near 0°C temperatures) condenser and liquid phase samples from a condenser bottle. These samples were analyzed using appropriate columns and analysis procedures, as described in the following sections.

Gaseous Phase Analysis

In order to analyze the composition of the effluent gas from the condenser bottle, this gas stream was directly introduced to the GC sample loop (6 μl volume of sample injection for each sampling). Standard gas was also purchased and connected to the GC. Since the temperature of

the condenser was maintained at near 0°C throughout the experiment, the effluent gas stream from the condenser bottle would not contain any hydrocarbons heavier than butane (boiling point: -0.5°C). To separate the permanent gas as well as light hydrocarbons, we used a 6 feet long stainless steel column packed with HayeSep Q packing material.

Fig. 12a shows the chromatogram of the standard gas separated using the HayeSep Q packed column and analyzed using a TCD detector. Composition of the standard gas is 1 % each of CH_4, CO, CO_2, C_2H_2, C_2H_4, and C_2H_6 in nitrogen. GC conditions for this analysis were: oven temperature; 50°C, detector temperature; 180°C, detector reference gas (helium) flow rate; 18 CC/min, and carrier gas flow rate (helium); 20 CC/min. The effluent gas stream from the condenser bottle were analyzed using the same GC conditions for the cracking of reference fuel (cetane, C_{17}) and diesel fuel. The chromatograms of GC analysis for cetane and diesel fuels are shown in Figs 12b and 12c, respectively, and summarized in **Table 5.**

These results indicate that the majority of the gas phase is composed of C_4-hydrocarbons (most likely butane). The nitrogen in the gas stream from the cracked diesel fuel may be from the compressed air in the fuel tank. A notable feature is that a relatively clean chromatogram was obtained from the reference fuel, whereas the chromatogram from diesel fuel has several complicated peaks in the C_1 - C_2 range.

Liquid Phase Analysis

GC analysis of the liquid samples in this experiments is much more complicated than gas phase sample analysis. One of reasons is that the product distribution is potentially very wide and products of C_5 - C_{17}, or higher hydrocarbons are possible. Furthermore, many kinds of unsaturated hydrocarbons, such as olefins, can be present and some of these hydrocarbons may become thermally cracked (become lighter hydrocarbons) or dimerized (become heavier hydrocarbons) during tests. Complete identification and/or quantification are beyond the scope of this program. Therefore, we analyzed the liquid phase samples, both condensed in the collector bottle at 0°C and remnant liquid phase after heating collector bottle at 100°C, only for qualitative information.

For the liquid phase GC analysis, we use a 60 m long, wide bore capillary column (Supelco product; SPB-1, 5μm film). A mixture of 19 hydrocarbons from propane (C_3H_8) to pentadecane ($C_{15}H_{32}$) were used as a standard sample. The same GC conditions were used throughout the liquid phase analysis, which were: (1) oven temperature 35°C (5 min) to 200°C at 20°C/min rate; (2) helium carrier gas flow 20 CC/min; (3) 20 CC/min TCD helium gas flow; and (4) 1.5 μl sample injection at 200°C. To remove any liquid phase contaminants from the previous tests, the column was heated to 250°C for 1 hr after each test. Results (chromatograms) of these tests are attached in the appendix and summarized in **Table 6.**

As expected, the 0°C liquid collect from both cetane (C_{17}) cracking and diesel cracking reactions comprises a wide range of hydrocarbons (from C_4 to C_{12}). For both cetane and diesel cracking reactions, C_6 is a dominant product (more than 30% in volume). Furthermore, it is clear that diesel cracking produces much more complex hydrocarbons and larger amounts of heavy

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Figure 12: GC Chromatograms of the Gas Phase Analyses. (a) Standard Sample;
(b) Effluent from Cetane Reaction; and (c) Effluent from Diesel Reaction.

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Table 5. Summary of Gas Phase GC Analyses[1]

Sample	Retention Time (min)	Area Percentage[2] (%)	Possible Chemical Compound
Standard Sample	0.43	91.13	N_2
	0.62	1.18	CH_4
	0.9	0.24	CO
	1.18	1.84	CO_2
	1.37	1.43	C_2H_2
	1.44	1.95	C_2H_4
	1.89	1.96	C_2H_6
Gas Phase From Cetane	0.46	0.21	N_2
	0.61	1.36	CH_4
	0.96	0.67	CO and/or CO_2
	1.38	5.7	C_2 Compounds
	1.82	3.4	C_2 Compounds
	5.33	9.7	C_3 (?) Compounds
	5.67	78.9	C_4 (?) Compounds
Gas Phase From Diesel	0.44	19.93	N_2
	0.6	1.01	CH_4
	0.97	0.06	CO and/or CO_2
	1.36	3.41	C_2 Compounds
	1.77	2.56	C_2 Compounds
	1.88	1.38	C_2 Compounds
	5.35	6	C_3 (?) Compounds
	5.67	65.58	C_4 (?) Compounds

1:   Using HayeSep Q packed column and analyzed using the TCD detectors
2:   Area percentage generally proportional to the concentration of the compounds

Table 6. Summary of Liquid Phase GC Analyses

Sample	Retention Time (min)	Area Percent. (%)	Possible Chemical Comp.	Retention Time (min)	Area Percent. (%)	Possible Chemical Comp.
Standard Sample	0.44	0.63	propane	7.2	1.8	octane
(Supelco	0.57	0.23	methylpropane	9.79	2.98	xylene
calibration mix	0.68	0.27	butane	10.5	4.17	propylbenzene
No. 4-8884)	0.91	0.45	methylbutane	11.16	3.68	decane
	1.22	0.89	pentane	14.01	18.76	butylbenzene
	1.49	6.6	methylpentane	19.29	37.37	dodecane
	1.66	4.81	hexane	19.44	1.57	tridecane
	2.44	2.77	dimethylpentane	21.09	0.83	tetradecane
	4.67	0.93	heptane	22.04	1.34	pentadecane
	6.67	8.51	toluene			
0°C collect from	0.5	14.89	C_4	15.18	6.02	C_{10}
cetane cracking	1.49	33.18	C_6	15.89	4.06	C_{10}
	6.55	11.19	C_7	17.07	8.45	$< C_{12}$
	11.81	2.59	C_{10}	17.72	2.74	$< C_{12}$
	14.24	16.88	C_{10}			
100°C remnant	10.68	29.03	C_9			
from cetane	13.97	70.97	C_{10}			
cracking						
0°C collect from	0.49	4.59	C_4	8.95	5.82	C_8
diesel cracking	0.56	2.18	C_4	9.68	5.06	C_9
	0.89	1.79	C_5	10.49	5.92	C_{10}
	1.17	2.92	C_5	11.24	5.56	C_{10}
	1.34	30.48	C_6	11.54	2.34	C_{10}
	4.78	2.2	C_7	11.85	2.93	C_{10}
	6.76	2.31	C_7	12.5	6.05	$< C_{12}$
	8.08	2.4	C_8	14.3	14.8	$< C_{12}$

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Table 6. Summary of Liquid Phase GC Analysis (continued)

Sample	Retention Time (min)	Area Percent. (%)	Possible Chemical Comp.	Retention Time (min)	Area Percent. (%)	Possible Chemical Comp.
100°C remnant from diesel cracking	0.62	10.86	C_4	11.44	42.19	C_{10}
	10.77	21.82	C_{10}	25.96	25.13	$>C_{15}$
		:			.	
Cetane (technical Grade)	0.26	0.53	$<C_3$	13.1	0.88	C_{11}
	0.6	2.1	C_4	14.12	2.28	C_{11}
	1.35	81.17	C_6	45.41	2.16	$>C_{15}$
	11.63	4.05	C_{10}	45.67	0.87	$>C_{15}$
	11.98	5.97	C_{10}			
Diesel (Exxon No. 2D)	0.38	2.5	$<C_3$	19.14	4.18	C_{12}
	1.41	54	C_6	20.71	2.52	C_{13}
	7.64	2.18	C_8	21.44	1.92	C_{14}
	8.05	2.11	C_8	29.74	1.5	$>C_{15}$
	11.62	2	C_{10}	31.54	4.04	$>C_{15}$
	11.8	2.31	C_{10}	34.91	1.46	$>C_{15}$
	13.48	2.19	C_{11}	36.4	3.66	$>C_{15}$
	15.48	13.44	C_{11}			

molecules than cetane cracking. For both cases, the heaviest molecule in the 0°C liquid collect is C_{12} (boiling point: 216°C (421°F)).

The dominant hydrocarbon molecule in 100°C remnants is C_{10} for both cetane and diesel cracking reactions. An interesting feature in this analysis is that some C_4 hydrocarbon (boiling point: less than 0°C (32°F)) is detected from the 100°C remnant in diesel cracking. We believe that this light hydrocarbon is a by-product of cracking reaction during GC analysis.

The chromatograms of technical grade cetane and commercial diesel (Exxon No.2D) shows the significance of the cracking of hydrocarbons during GC analyses. For both cetane and diesel, C_6 was a dominant constituent. However, in both cases, we can detect very heavy hydrocarbons, probably C_{17}, which have a retention time greater than 35 min. We have not observed any molecules exhibiting retention times greater than 26 min from any other liquid samples collected from catalytic cracking reactions. Comparing the GC chromatograms from

cetane, diesel, and other liquid samples from catalytic cracking, we can conclude that most of the fuel fed is successfully converted into light hydrocarbons and the amount of unconverted fuel vapor, if any, is negligible.

6.   Space Velocity Consideration

Space velocity, which is defined as the lbs/hr of total feed (in this case diesel fuel) divided by the total pounds of catalysts holdup in the reaction zone , is an important variable in the catalytic process. As discussed in the previous section, it required about 0.11 lbs of catalysts (4.36 inch^3 volume) to treat 0.2 GPH of diesel fuel, which corresponds to 12.91 lbs/hr/lb of weight space velocity. Therefore, if we have to process 0.5 GPH of diesel fuel, with current catalysts, we need at least 0.275 lb (10.9 inch^3 volume of catalysts in a loosely packed state) of catalyst. In the P.I.'s opinion, if we further optimize the catalytic cracking process as well as catalyst chemistry, we can increase space velocity further (less catalyst needed).

7.   Energy Required for Catalytic Cracking Process

Overall catalytic cracking is an endothermic reaction, although there are many secondary reactions, such as isomerization, polymerization, and coking, that can be exothermic or endothermic depending on the reactor (reaction) temperatures and pressures. It is not possible to estimate theoretically the amount of heat of reactions, but we can determine experimentally the energy consumed in the reactor to achieve catalytic cracking of diesel to gaseous hydrocarbons.

In the experimental system shown in **Fig. 10**, we measured the power input to the reactor where temperature was maintained at 350°C (662°F) using a proportional band type-power supply. We also measured the power input to the tape preheater at 260°C (500°F) using a variable transformer power supply. Without any fuel flowing (blank run), the reactor and the preheater required 85.8 W-hr (29.3 Btu) and 58.6 W-hr (20 Btu) of energy to maintain the temperature at 350°C (see **Fig. 13a**) and at 260°C, respectively. In a blank run, most of this energy should have been consumed as a form of heat energy loss from the surfaces of the heater by convection and radiation. As we introduced the diesel fuel into the catalytic cracking reactor, the power required by the reactor increased accordingly. For example, the heat energy required by the reactor was 205.2 W-hr (70 Btu) and 289.2 W-hr (98.6 Btu) for the diesel flow rates of 0.085 GPH and 0.2 GPH, respectively (see **Fig. 13b and c**). The heat energy for preheater also was increased to 139 W-hr (47.4 Btu) for a fuel flow rate of 0.2 GPH. These results are summarized in **Table VII**.

Without considering heat loss at the heater, the total energy required for diesel cracking both for preheater and reactor is 146 Btu for 0.2 GPH of fuel flow which corresponds to 730 Btu per GPH of diesel fuel. If we subtract the amount of energy required for a blank run (both for preheater and reactor), actual energy required for the catalytic cracking process can be calculated as 96.7 Btu for 0.2 GPH or 483.5 Btu per GPH of diesel flow. This value is significantly lower than the heat of vaporization of diesel (about 781 Btu/gallon). This result implies that catalytic cracking of diesel is a much less energy intensive process than vaporization of diesel for clean combustion.

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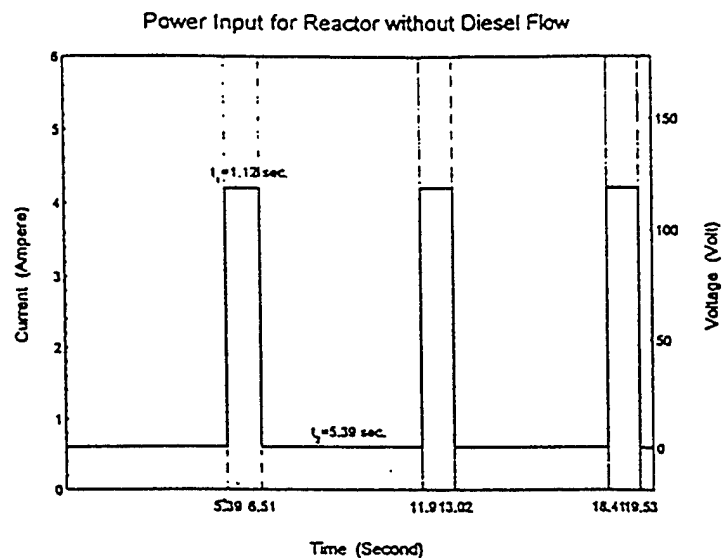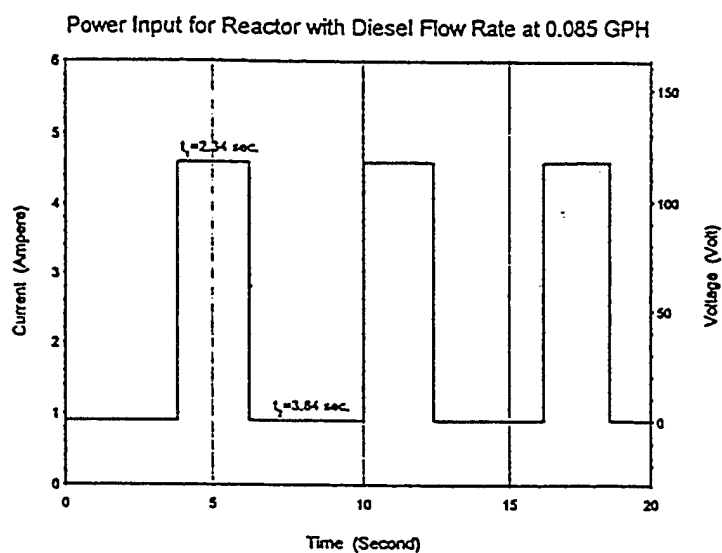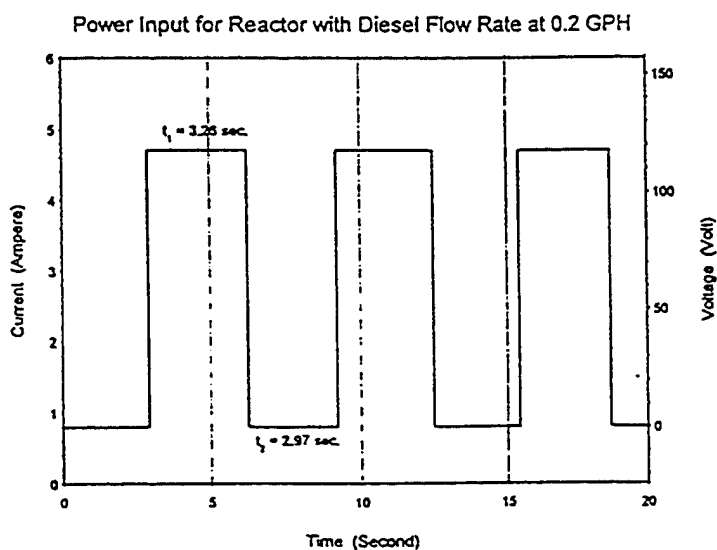
Figure 13: Electric Power vs Time Profiles for the Catalytic Cracking Reactor at 350°C. (a) Blank Run; (b) 0.085 GPH of Diesel Flow; and (c) 0.2 GPH of Diesel Flow.

Table 7. Energy Required for Catalytic Cracking Process

Fuel Flow Rate	Heat Input Measured (Btu)		
	Preheater at 260°C (500°F)	Reactor at 350°C (662°F)	Total Heat Input
Blank Run (No Fuel Flow)	20	29.3	49.3
0.085 GPH Diesel Flow	33.7	70	103.7
0.2 GPH Diesel Flow	47.4	98.6	146
Heat Require to process 1 GPH of Diesel with Heat Loss	237	493	730
Heat Require to process 1 GPH of Diesel without Heat Loss	137	346.5	483.5

8.   Conclusions

During the Phase I program, Aspen Systems, Inc. successfully demonstrated the feasibility of producing gaseous fuel from diesel via a catalytic cracking process. Clean combustion of diesel and wide ranges of firing rate controllability were clearly demonstrated using the M-3 burner head. The total energy required for 1 gallon of diesel fuel cracking operation is determined to be 680 Btu and 730 Btu (with and without the heat loss incurred during the operation) which is less than the energy required for vaporization of diesel (theoretically 781 Btu/gallon).

During this research, we realized that the best performing catalyst for the catalytic cracking of diesel for our operating conditions is different from those used in the industry for cracking of heavy hydrocarbons. Furthermore, we found that slight modification of the commercial catalyst was necessary to achieve high conversion efficiency of diesel to gaseous fuel. We believe that we can develop better performance catalysts for the catalytic cracking of diesel by further research along this line.
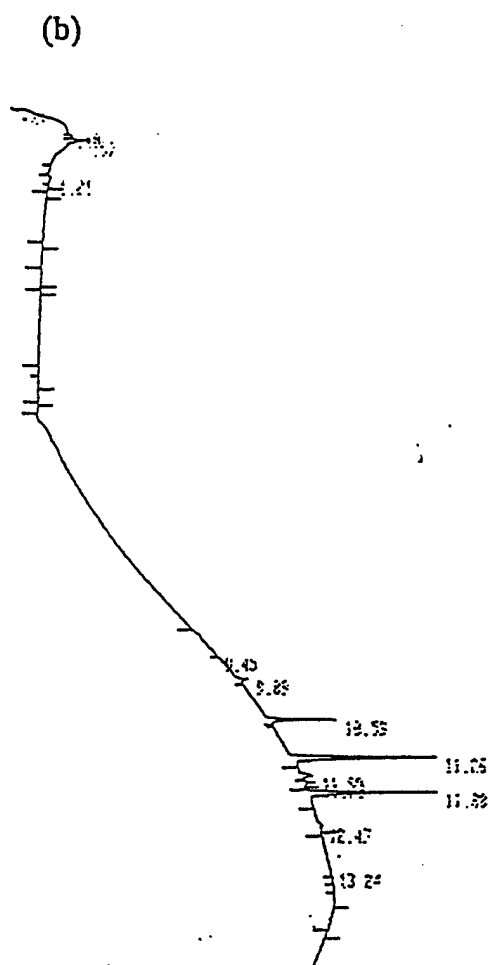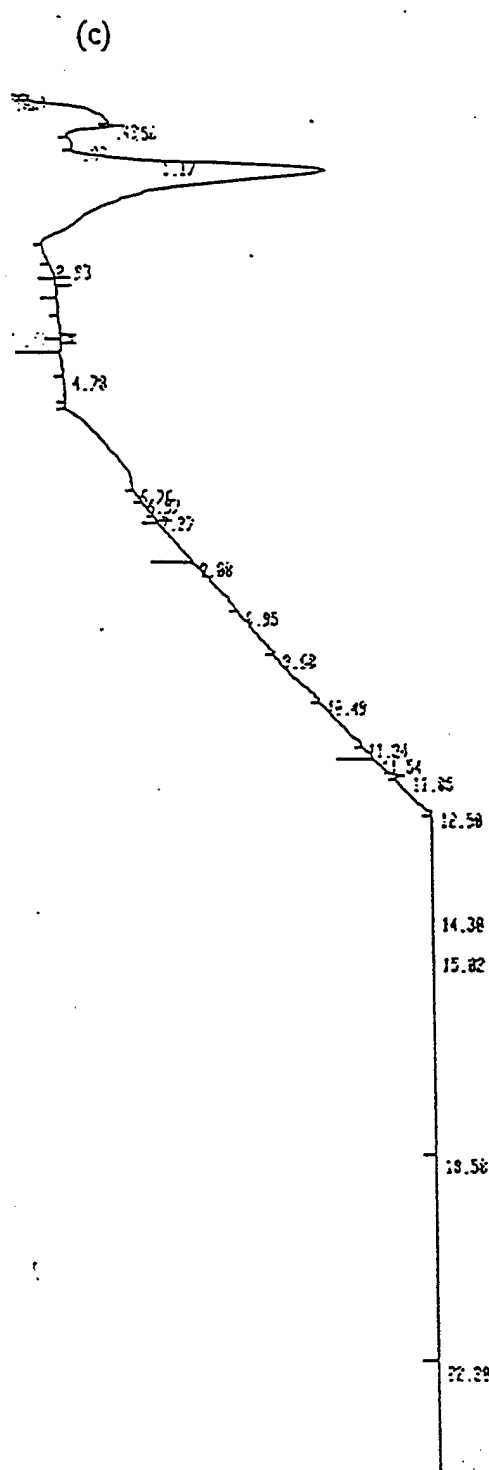
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APPENDIX: GC CHROMATOGRAMS FOR LIQUID PHASE ANALYSES
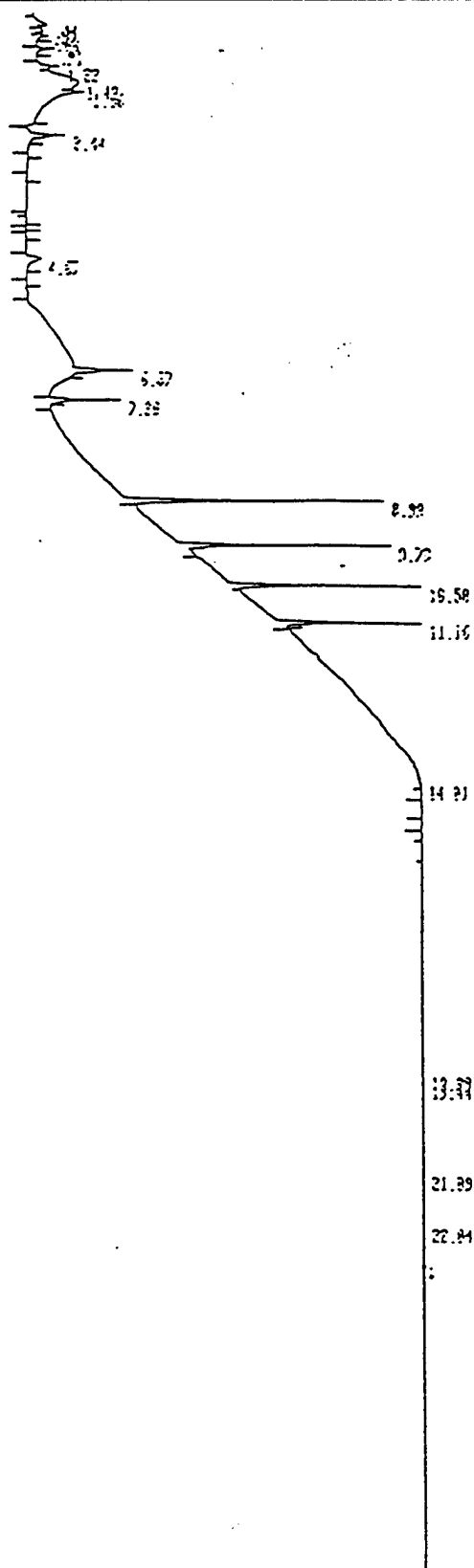
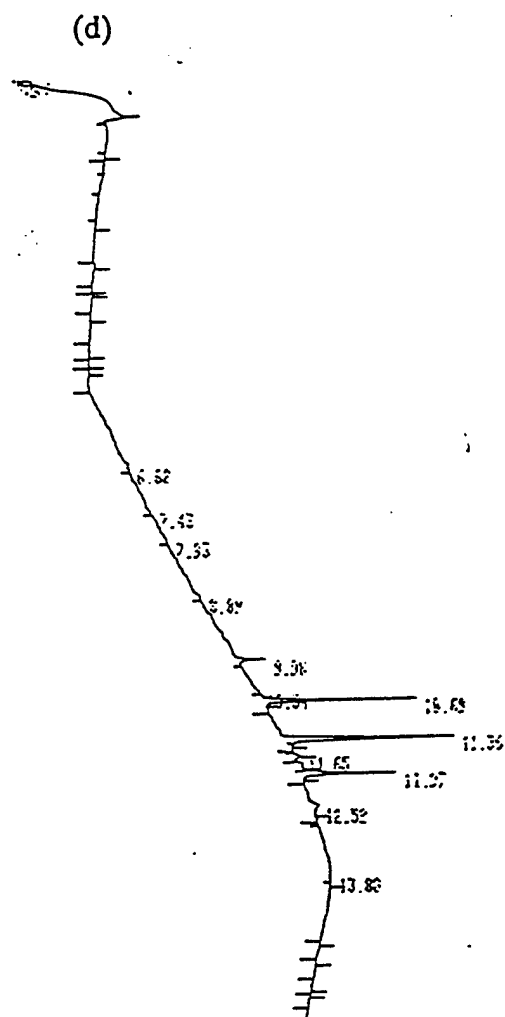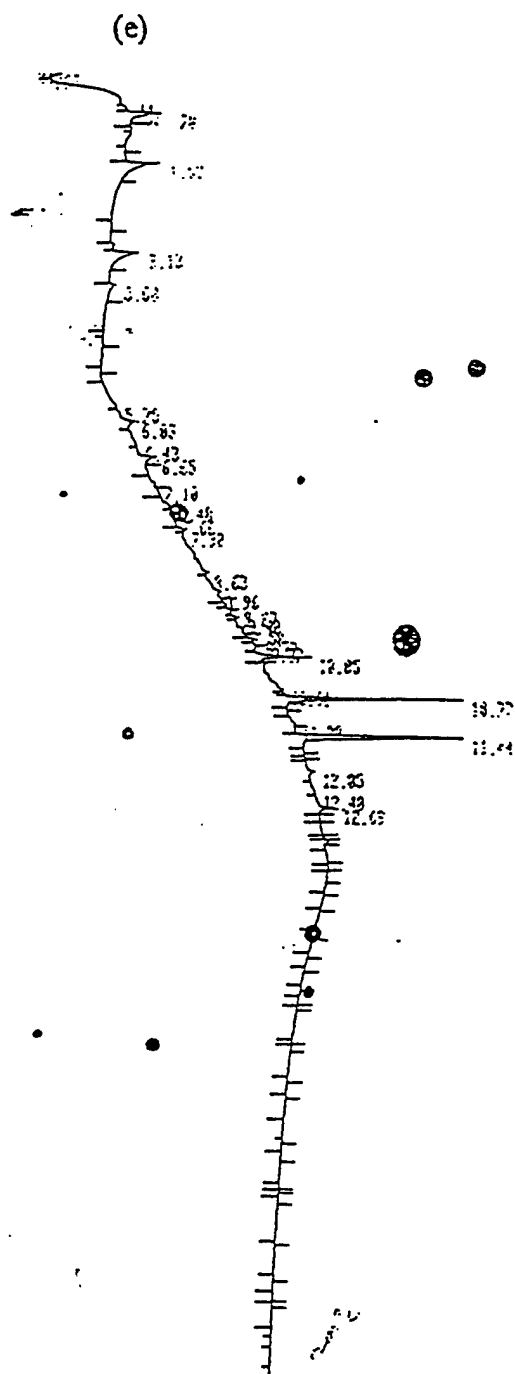(a) Standard Sample (Supelco Calibration Mix No 4-8884)

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(c)   (b)

STOP

RUN #   5

AREA%
   RT   AREA TYPE   AR/HT   AREA%
  8.46   18925   PV   8.253   19.648
  8.57   13565   VV   8.231   24.387
 18.59   7983   VV   8.809   14.288
 11.25   14861   VB   8.837   23.278
 11.88   9171   BB   8.836   16.497

TOTAL AREA=   55625
MUL FACTOR= 1.8988E+88

(b) 0°C Collect from Cetane; (c) 0°C Collect from Diesel.

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(d) 100°C Residue from Cetane; (c) 100°C Residue from Diesel.
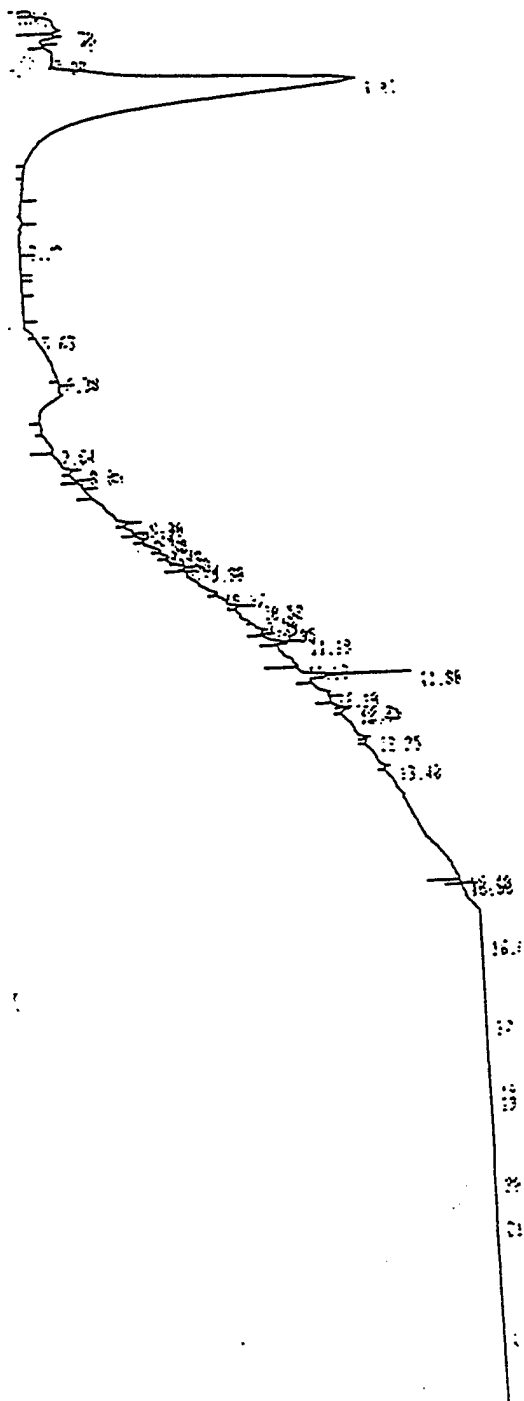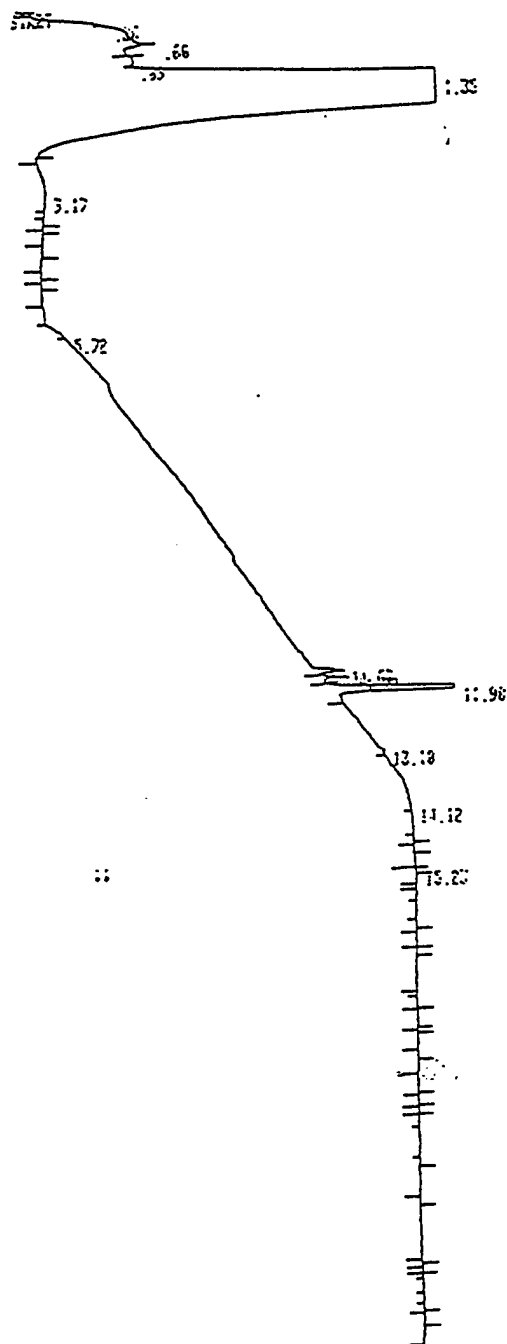
(f) From Technical Grade Cetane; (g) From Diesel (No. 2D).